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PATENT SPECIFICATION

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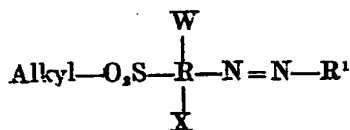
COMPLETE SPECIFICATION

Monoazo Dyestuffs and process for their manufacture

We, SANDOZ LTD., of Basle, Switzerland, a Body Corporate organised according to the laws of Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The object of the present invention is to produce monoazo dyestuffs which draw onto acetate rayon, polyamide or polyester fibres in pure yellow to orange coloured shades and whose dyeings excel with excellent fastness to light, washing and sublimation and which are also fast towards combustion gases, hereinafter referred to as gas fumes.

The monoazo dyestuffs produced according to the present invention have the composition

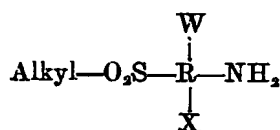


wherein R denotes a benzene or naphthalene residue, W denotes a hydrogen atom or a —SO₂— alkyl group and X denotes a hydrogen, chlorine, bromine or fluorine atom or an alkyl fluoroalkyl or —SO₂— alkyl group, and R¹ denotes the radical of a tertiary aminobenzene compound which is free from halogen atoms and may possess in meta-position to the tertiary amino group an alkyl group and in which a cyanoalkyl group is attached to the nitrogen atom, the other substituent being alkyl or hydroxyalkyl.

"Alkyl" denotes throughout the specification an alkyl group containing at least one and at most three carbon atoms.

The new monoazo dyestuffs are obtained by coupling one molecular proportion of the diazo compound of an amine of the

benzene or naphthalene series which corresponds to the general formula



wherein R denotes a benzene or naphthalene residue, W denotes a hydrogen atom or a —SO₂— alkyl group, and X denotes a hydrogen, chlorine, bromine or fluorine atom or an alkyl fluoroalkyl or —SO₂— alkyl group, with one molecular proportion of a tertiary aminobenzene compound which is free from halogen atoms and may possess in meta-position to the tertiary amino group an alkyl group and in which a cyanoalkyl group is attached to the nitrogen atom, the other substituent being alkyl or hydroxyalkyl,

It is already known to couple diazotised aminobenzenes containing at least one alkyl sulphone group but devoid of nitro or water-solubilising groups, with tertiary amines of the benzene series. Amongst the azo components which may be used to carry out this reaction may for example be mentioned: N:N-dimethylaminobenzene, N:N-diethylaminobenzene, N-ethyl-N-hydroxyethylaminobenzene, N-ethyl-N-methoxyethylaminobenzene, or 1-(N:N-dimethoxy-ethyl)-amino-2-methoxy-5-methylbenzene, when yellow to orange red dyestuffs are obtained which partly dye acetate rayon only very badly and whose dyeings inasmuch as the dyestuffs draw on to acetate rayon are insufficiently fast to light. On the other hand it is already known that diazotised nitro amino benzenes containing one alkyl sulphone group but devoid of water solubilising groups, can be coupled with tertiary amines of the benzene series in which at least one cyano-

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alkyl group is attached to the nitrogen atom. According to the latter process there are, however, obtained dyestuffs which dye acetate rayon in blueish tinged red tints. The shades of these products on polyamide fibres differ from those on acetate rayon and are much inferior in their fastness to light.

All the disadvantages of the above mentioned processes known hitherto—viz. poor drawing capacity onto acetate rayon, insufficient fastness to light and undesired shades on polyamide fibres—are now removed by the process according to the present invention which allows the production of dyestuffs which draw well onto acetate rayon and which dye these and polyamide fibres in pure yellow to orange shades of deep colour of excellent fastness to light. The other fastnesses are also very good as mentioned above. It is quite surprising that by introducing a cyanoalkyl group into the azo component used in the first of the above mentioned known processes, the drawing capacity of the new dyestuffs could be considerably improved in many cases.

It is furthermore a remarkable fact that the dyestuff obtained according to the process of the present invention allow the dyeing of fabrics made from cellulose acetates and polyamide fibres in the same shade without impairing the fastness to light to a considerable extent.

Amongst the amines of the benzene or naphthalene series which may be used for the preparation of the diazo compounds the following may, for example, be mentioned: alkylsulphonyl-aminobenzenes, alkylsulphonyl-chloro-aminobenzenes, alkylsulphonyl-bromo-aminobenzenes, alkylsulphonyl-fluoro-aminobenzenes, alkylsulphonyl-alkyl-aminobenzenes, alkylsulphonylfluoroalkyl-aminobenzenes, di-(alkylsulphonyl)-aminobenzenes, di-(alkylsulphonyl)-chloro-aminobenzenes, di-(alkylsulphonyl)-bromo-aminobenzenes, di-(alkylsulphonyl)-fluoro-aminobenzenes, tri-(alkylsulphonyl)-aminobenzenes or, if required, further substituted alkylsulphonyl-aminonaphthalenes.

As azo components the following are, for example suitable:—N-methyl-N-cyanoethyl-aminobenzene, N-ethyl-N-cyanoethyl-aminobenzene, N-hydroxyethyl-N-cyanoethyl-aminobenzene, N-hydroxypropyl-N-cyanoethyl-aminobenzene, 1-(N-methyl-N-cyanoethyl)-amino-3-methylbenzene, 1-(N-ethyl-N-cyanoethyl)-amino-3-methylbenzene, 1-(N-hydroxyethyl-N-cyanoethyl)-amino-3-ethylbenzene, 1-(N-hydroxypropyl-N-cyanoethyl)-amino-3-methylbenzene, 1-N-methyl-N-cyanomethyl-aminoben-

zene, N-ethyl-N-cyanomethylaminobenzene or N-hydroxyethyl-N-cyanomethylaminobenzene.

Coupling of the diazo compound with the azo component is carried out in the usual manner, preferably in an acidic aqueous medium. The monoazo dyestuffs which precipitate are filtered off, washed and dried.

The following examples illustrate the invention without limiting it. The amounts and conditions of temperatures may be varied in some cases to a large extent within the scope of the above mentioned description. The parts are by weight and the temperature is expressed in degrees Centigrade.

EXAMPLE 1.

10.3 parts of 1-amino-2-chloro-4-methylsulphonylbenzene are diazotised in the usual manner at 60° with 3.5 parts of sodium nitrite in 65 parts of concentrated sulphuric acid. The reaction mixture is then poured onto 350 parts of ice and 75 parts of water. A solution of 10 parts of N-hydroxyethyl-N-cyanoethyl-aminobenzene in 10 parts of concentrated hydrochloric acid and 25 parts of water is now added dropwise. When coupling is completed the monoazo dyestuff formed is filtered off, washed free from acid and dried.

If the dyestuff is dispersed in the usual manner it dyes acetate rayon and polyamide fibres in deep yellow tinged orange tints of excellent fastness to light and very good fastness to wet treatments. If the 10.3 parts of 1-amino-2-chloro-4-methylsulphonylbenzene are replaced by 12.5 parts of 1-amino-2-bromo-4-methylsulphonylbenzene then a dyestuff of similar properties is obtained.

EXAMPLE 2.

If the azo component mentioned in example 1 is replaced by 1-(N-hydroxyethyl-N-cyanoethyl-amino-3-methylbenzene then a similar dyestuff is obtained.

EXAMPLE 3.

If the 10.3 parts of 1-amino-2-chloro-4-methylsulphonylbenzene mentioned in the previous examples are replaced by 10.3 parts of the isomeric 1-amino-2-methylsulphonyl-4-chlorobenzene then a dyestuff is obtained which also dyes acetate rayon with a yellow tinged orange colour.

EXAMPLE 4.

12.5 parts of 1-amino-4-bromo-2-methylsulphonylbenzene are diazotised in the manner described above. After pouring the diazo solution onto ice water it is coupled with a solution of 10.5 parts of 1-(N-hydroxyethyl-N-cyanoethyl)-amino-3-methylbenzene in 10 parts of concentrated hydrochloric acid and 25

parts of water. The dyestuff formed is worked up in the usual manner. It dyes acetate rayon in deep yellow tinged orange tints of good fastness to light.

EXAMPLE 5.

6.2 parts of 1-amino-2:4-di-(methylsulphonyl)-benzene are stirred into 6.3 parts of concentrated hydrochloric acid and 10 parts of water for some time and then diazotised in the presence of 20 parts of ice and 1.75 parts of sodium nitrite. The diazo compound is coupled with 5 parts of N-hydroxyethyl-N-cyanoethyl-amino-benzene dissolved in a mixture of 50 parts of water, 5 parts of concentrated hydrochloric acid and 50 parts of ice. The dyestuff formed is filtered off, washed free from acid and dried.

If the dyestuff is dispersed in the usual manner it dyes acetate rayon with brilliant orange tints of excellent fastness to light, washing, gas fumes and sublimation.

EXAMPLE 6.

7.6 parts of sodium nitrite are added within 1 hour at 60° to 90 parts of concentrated sulphuric acid. The solution is cooled to 10—20° and diluted with 100 parts of concentrated acetic acid whereupon 24.9 parts of 1-amino-2:4-di-(methylsulphonyl)-benzene are added at 10—15°. 100 parts of concentrated acetic acid are then added dropwise and the excess nitrite is destroyed with 5 parts of urea. The diazo solution is poured onto 350 parts of ice and coupled with a solution of 21 parts of 1-(N-hydroxyethyl-N-cyanoethyl-amino-3-methylbenzene in 200 parts of water, 100 parts of ice and 20 parts of 30% hydrochloric acid. The dyestuff formed is filtered off, washed free from acid and dried. It dyes acetate rayon with red-orange tints of very good fastness properties.

EXAMPLE 7.

If in example 6 the 21 parts of the azo component 1-(hydroxyethyl-N-cyanoethyl)-amino-3-methylbenzene are replaced by 18 parts of N-ethyl-N-cyanoethyl-amino-benzene then a dyestuff of similar properties is obtained.

EXAMPLE 8.

If in example 6 the azo component is replaced by 21 parts of N-hydroxypropyl-N-cyanoethyl-amino benzene then a dyestuff is obtained which also dyes acetate rayon in deep red-orange tints of very good fastness properties.

EXAMPLE 9.

5 parts of sodium nitrite are added at 60° to 60 parts of concentrated sulphuric acid. The solution is cooled to 10—20° and diluted at this temperature with 65 parts of concentrated acetic acid. 15 parts of 1-amino-4-methylsulphonylnaphtha-

lene are gradually added at 10—15° and a further 65 parts of concentrated acetic acid are then added to the solution. After 1 hour the excess nitrite is neutralised with 3 parts of urea and the diazotisation mixture is poured onto 750 parts of ice. The suspension now present is neutralised with 135 parts of crystalline sodium acetate and then coupled with a solution of 13 parts of N-hydroxyethyl-N-cyanoethyl-amino-benzene in 150 parts of water and 14 parts of 30% hydrochloric acid. The dyestuff obtained dyes acetate rayon and polyamide fibres in deep orange tints of very good fastness properties.

EXAMPLE 10.

If in example 9 the 13 parts of N-hydroxyethyl-N-cyanoethylaminobenzene are replaced by 14 parts of 1-(N-hydroxyethyl-N-cyanoethyl)-amino-3-methylbenzene then a dyestuff is obtained which dyes polyamide fibres in particular in yellowish tinged scarlet red tints of extraordinary fastness to light and very good fastness to wet treatments.

EXAMPLE 11.

17.1 parts of 1-amino-4-methylsulphonylbenzene are stirred into 50 parts of concentrated acetic acid and then poured onto 150 parts of ice and 30 parts of 30% hydrochloric acid. One diazotises at 0° with a solution of 7 parts of sodium nitrite and 30 parts of water. 20 parts of N-hydroxyethyl-N-cyanoethyl-amino-benzene are added to the diazo solution when a dyestuff is formed which dyes in reddish tinged yellow tints of very good fastness properties.

EXAMPLE 12.

0.6 parts of the dyestuff obtained according to the method described in example 1 are dispersed with the aid of Turkey Red oil and dyed onto 100 parts of acetate rayon in a soap bath in the usual manner, preferably at raised temperatures. Pure orange coloured tints of excellent fastness properties are obtained. In order to improve the dispersion, the dyestuff can be ground prior to the dyeing process with suitable wetting agents, dispersing agents or emulsifiers, preferably in the presence of inorganic salts such as sodium sulphate.

EXAMPLE 13.

10 parts of a 20% aqueous paste of the dyestuff obtained according to the method described in example 1 are thoroughly mixed with 10 parts of diethylene glycol and 80 parts of gum arabic. The printing paste obtained yields after steaming on acetate rayon and polyamide fibres orange coloured prints of excellent fastness properties.

EXAMPLE 14.

5 parts of sodium nitrite are added at

60° to 65 parts of concentrated sulphuric acid. After the conversion to nitrosyl sulphuric acid is completed, 15 parts of 1-amino-5-methyl-sulphonylnaphthalene are added at 15-20° to the solution which has been diluted with 65 parts of concentrated acetic acid and subsequently another 65 parts of concentrated acetic acid are added. After 1 hour the excess nitrite is destroyed with 3 parts of urea and the diazo mixture is then poured onto 500 parts of ice and 1500 parts of water. A solution of 13 parts of N-hydroxyethyl-N-cyanoethyl-aminobenzene in 16 parts of 30% hydrochloric acid and 150 parts of water is now added dropwise to the diazo solution obtained. The dyestuff precipitates after some time as a dark red suspension. It is worked up in the usual manner and dyes acetate rayon and polyamide fibres in orange coloured tints.

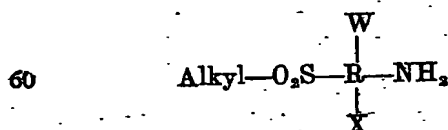
EXAMPLE 15.

5 parts of sodium nitrite are added at 60° to 65 parts of concentrated sulphuric acid. After the conversion to nitrosyl sulphuric acid is completed, 20 parts of 1-amino-2-bromo-4-methyl-sulphonylnaphthalene are added at 15-20° to the solution which has been diluted with 65 parts of concentrated acetic acid. The diazo mixture is subsequently diluted again with 65 parts of concentrated acetic acid. After one hour the excess nitrite is destroyed with 3 parts of urea and the mixture is poured onto 500 parts of ice and 1500 parts of water. A solution of 13 parts of N-hydroxyethyl-N-cyanoethyl-aminobenzene in 16 parts of 30% hydrochloric acid and 150 parts of water is added dropwise to the diazo solution obtained. A dark red dyestuff is soon formed which, when worked up in the usual manner, dyes acetate rayon and polyamide fibres in orange coloured tints.

If the azo component in this example is replaced by 14 parts of 1-(N-hydroxyethyl-N-cyanoethyl)-amino-3-methylbenzene then a scarlet red powder is obtained which dyes acetate rayon and polyamide fibres in slightly more reddish-tinted tints.

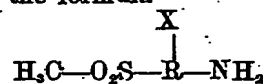
What we claim is:—

1. A process for the preparation of monoazo dyestuffs characterised in that one molecular proportion of the diazo compound of an amine of the benzene or naphthalene series which corresponds to the general formula



wherein R denotes a benzene or naphthalene residue, W denotes a hydrogen atom or a —SO₂—alkyl group and X denotes a hydrogen, chlorine, bromine or fluorine atom or an alkyl fluoroalkyl or —SO₂—alkyl group, is coupled with one molecular proportion of a tertiary aminobenzene compound which is free from halogen atoms and may possess in meta-position to the tertiary amino group an alkyl group and in which one cyanoalkyl group is attached to the nitrogen atom, the other substituent being alkyl or hydroxyalkyl.

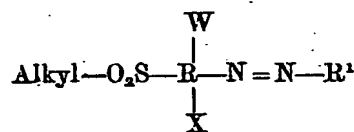
2. A process according to claim 1 in which the amine of the benzene or naphthalene series is an amine which corresponds to the formula



wherein R denotes a benzene or naphthalene residue and X denotes a hydrogen, chlorine or bromine atom or a —SO₂—CH₃ group, and in which the tertiary aminobenzene compound is a N-cyanoalkyl-N-alkyl-aminobenzene, or a N-cyanoalkyl-N-hydroxyalkylaminobenzene, whose benzene nuclei may be substituted by an alkyl group.

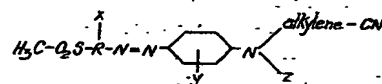
3. A process for the preparation of monoazo dyestuffs substantially as herein described.

4. The monoazo dyestuffs which correspond to the general formula



wherein R, W and X have the significance shown in claim 1, and R¹ denotes the radical of a tertiary aminobenzene compound which is free from halogen atoms and may possess in meta-position to the tertiary amino group an alkyl group and in which a cyanoalkyl group is attached to the nitrogen atom, the other substituent being alkyl or hydroxyalkyl.

5. The monoazo dyestuffs which correspond to the general formula



wherein R and X have the significance shown in claim 2 and Y denotes a hydrogen atom or an alkyl group in the meta position to the tertiary amino group, and wherein Z denotes an alkyl group or an hydroxyalkyl group.

6. The particular monoazo dyestuffs herein described.

5 7. A dyeing or printing process in which a dyestuff as claimed in any one of claims 4 to 6 is used to dye or print acetate rayon, polyamide or polyester fibres.

8. A dyeing process conducted substantially as described in example 12 herein.

9. A printing process conducted sub-

stantially as described in example 13 10 herein.

10. Acetate rayon, polyamide or polyester fibres whenever dyed or printed according to the processes claimed in any of claims 7, 8 or 9.

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